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Dynamics of Crossover Phenomenon in Phase-Separating Systems

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A new systematic theory for the dynamics of phase separation of quenched binary systems in a metastable state is presented. Not only the kinetic equation for the single-droplet size distribution function but also the linear equation with the source term for the dynamic structure function are derived from a unifying point of view. Three characteristic stages with two crossovers in time exponents are shown to exist after the nucleation stage. The dynamical scaling behavior and the time exponents are thus explored explicitly.

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The purpose of this Letter is to study the dynamics of phase separation in quenched binary systems in a metastable state, and thus to investigate the dynamical scaling behavior and the crossover phenomenon in first-order phase transitions from a unifying point of view. When the system is quenched into the two-phase region near the coexistence curve from the one-phase region, it undergoes phase separation by nucleation and growth of droplets of the minority phase. In this paper we consider only cases where the interfacial surface energy provides the only driving force for the coarsening and ignore the other forces, such as elastic interactions. Then, there are two kinds of growth mechanisms [1,2]. One is a direct growth from a supersaturated solution, where the number density of droplets does not change. Another is a growth due to the Ostwald ripening (or coarsening) where the larger droplets grow at the expense of the smaller ones which disappear. This leads to the reduction of the number density but does not change the volume fraction. After the nucleation stage, therefore, there are three characteristic stages [1-4]. The first is a growth stage (G) where the diffusive interactions among droplets are not important and hence the droplets grow directly and independently from the solution. The number density of the droplets does not change and the volume fraction of the droplets increases rapidly. After this stage the two kinds of growth mechanisms compete with each other through the diffusive long-range interactions. This is an intermediate stage (I) where the growth is no longer independent and is slowed down by the long-range interactions. The final stage is a coarsening stage (C) where the growth is governed only by the coarsening and the volume fraction becomes constant. Many experimental [1,4-8], numerical [9-11], and theoretical [12-15] approaches have been applied to study the crossover phenomena from the intermediate stage to the coarsening stage. In contrast to the study of the coarsening stage [16-19], however, the dynamical aspects of the intermediate stage are not yet well understood theoretically, although this stage is important for real systems [1,4-8].

In this Letter, we present a systematic theory for the

dynamics of crossover phenomena in phase-separating systems [2]. We consider a three-dimensional classical system which consists of spherical droplets of the minority phase and a supersaturated solution of the majority phase. The system has three characteristic lengths: the average droplet radius $\langle R \rangle(t)$, the interdroplet distance $L(t) = [4\pi n(t)/3]^{-1/3}$, and the screening length $l(t) = [4\pi n(t)\langle R \rangle(t)]^{-1/2}$, within which droplets have correlations, where $n(t)$ denotes the number density of droplets.

The supersaturated solution is described by the diffusion equation with the Gibbs-Thompson relationship as the boundary condition and the appropriate initial conditions. By solving such a diffusion equation and using mass conservation for each droplet, one can then derive the following rate equation for the radius of the i th droplet, on the length scale of order l [2]:

$$\frac{d}{dt} R_i(t) = \frac{aD}{R_i(t)^2} M_i(t), \quad (1)$$

with the source/sink strength

$$M_i(t) = \frac{R_i(t)}{R_0} - 1 - 4\pi a D R_i \times \sum_{j \neq i}^N \int_0^t ds \frac{\exp[-|\mathbf{X}_i - \mathbf{X}_j|^2/4Ds]}{(4\pi Ds)^{3/2}} M_j(t-s), \quad (2)$$

where N is the initial total number of droplets, \mathbf{X}_i the position vector from the origin to the center of the i th droplet, D the diffusion constant, a the capillary length, and $R_0 = a/\Delta_0$ the initial crucial radius, Δ_0 being the initial supersaturation. Here Eq. (1) is supplemented by the conservation of total mass,

$$\Phi(t) + \Delta(t) = \Phi_0 + \Delta_0 = Q, \quad (3)$$

where $\Phi(t)$ represents the volume fraction of droplets, $\Phi_0 = \Phi(0)$, and Q the total initial supersaturation. We assume that Q is small. Hence we have the small parameter $\langle R \rangle/l \sim \Phi^{1/2} \sim Q^{1/2} \ll 1$.

Equation (1) is a new starting equation to study the phase-ordering dynamics in the metastable system. The

third term of Eq. (2) represents the many-body effect due to the diffusive long-range interactions among droplets separated by a distance of order l and contains the higher-order terms in $\Phi^{1/2}$. Because of such interactions, one can solve Eq. (1) only numerically by computer simulations [2]. By employing the systematic expansion method in powers of $\Phi^{1/2}$, however, one can further manipulate it to obtain two kinds of macroscopic equations which one can reasonably analyze [2,18]. The first

is a kinetic equation for the single-droplet distribution function $f(R,t)$ with radius R , which is measured by an electron microscope [20]. The second is an equation for the dynamic structure function $S(\mathbf{k},t)$, which is observable by using small-angle scattering of neutrons, x rays, or light [17].

It is convenient to introduce the dimensionless time τ and radius a by $\tau = aDt/R_0$ [3] and $a = R/R_0$. Up to order $\Phi^{1/2}$, one can then find the following Fokker-Planck type kinetic equation, in dimensionless form:

$$\frac{\partial}{\partial \tau} f(a, \tau) = \frac{1}{\langle a \rangle^3} \frac{\partial}{\partial \rho} \frac{1}{\rho^2} \left[\lambda(\tau) + \left(\frac{3\Phi}{\mu_3} \right)^{1/2} \left\{ -\rho \langle \rho \lambda \rangle + \frac{\langle \lambda^2 \rangle}{\beta \mu_{-1}} \rho \frac{\partial}{\partial \rho} \frac{1}{\rho} \right\} \right] f(a, \tau), \quad (4)$$

with the screening term

$$\lambda(a, \tau) = 1 - \beta(\tau)\rho, \quad (5)$$

$$\beta(\tau) = \langle a \rangle(\tau) \left[1 + 3 \int_0^{\tau/\tau_s} v(\tau_s x) \langle \lambda \rangle(\tau_s x) dx \right], \quad (6)$$

where $\tau_s = \Delta_0 \langle a \rangle(0)^3 / \Phi_0$ is the screening time, $v(\tau) = n(\tau)/n(0)$ the normalized number density, $\rho = a/\langle a \rangle$, and $\mu_m(\tau) = \langle \rho^m \rangle$. The volume fraction is given by $\Phi(\tau) = \Delta_0 v(\tau) \langle a^3 \rangle(\tau) / \tau_s$, where the brackets denote the average over $f(R, \tau)$. The second term of Eq. (6) represents the static many-body (screening) effect of order Φ^0 and becomes important on the time scale of order τ_s . The term with $\Phi^{1/2}$ in Eq. (4) is the dynamic many-body (correlation) effect and becomes important on the time scale of order $\tau_s / \Phi^{1/2}$.

From Eq. (4), the distribution function $f(a, \tau)$ is shown to satisfy the scaling

$$f(a, \tau) = [n(\tau)/\langle R \rangle(\tau)] F(\rho, \tau), \quad (7)$$

with the temporal power laws

$$\langle a \rangle \sim \tau^{\eta_R}, \quad v \sim \tau^{-\eta_n}, \quad \Phi \sim \tau^{\eta_\Phi}, \quad (8)$$

where $\eta_\Phi = 3\eta_R - \eta_n$. The relative droplet size distribution function $F(\rho, \tau)$ satisfies the boundary conditions

$$\int_0^\infty F(\rho) d\rho = \int_0^\infty \rho F(\rho) d\rho = 1. \quad (9)$$

From Eq. (4), one can also find the growth laws

$$\frac{d}{d\tau} \langle a^3 \rangle = \mu_3 K(\tau) - 3\langle \lambda \rangle \left[1 - \frac{(3\Phi/\mu_3)^{1/2}}{\beta} \right], \quad (10)$$

$$\frac{d}{d\tau} \ln v(\tau) = -\frac{K(\tau)}{\langle a \rangle^3}, \quad (11)$$

with the coarsening rate

$$K(\tau) = \lim_{\rho \rightarrow 0} F(\rho, \tau) / \rho^2. \quad (12)$$

As is seen from Eqs. (10) and (11), there are two kinds of growth mechanisms. One is the growth from the solution which is described by the term $\langle \lambda \rangle(\tau)$. Another is the growth due to the coarsening which is described by the term $K(\tau)$. Thus, there are three characteristic

stages, G, I, and C:

$$(G) \quad 1 \ll \tau < \tau_s: \quad K=0, \quad \langle \lambda \rangle \sim -\langle a \rangle, \quad v=1,$$

$$(I) \quad \tau_s \leq \tau < \tau_c: \quad K \sim -\langle \lambda \rangle \sim -\langle a \rangle^{-1}, \quad v \sim \tau^{-2/3},$$

$$(C) \quad \tau \geq \tau_c: \quad K \sim K(\infty), \quad \langle \lambda \rangle \sim -\langle a \rangle^{-1}, \quad v \sim \tau^{-1}.$$

Here the coarsening time τ_c , over which Φ becomes nearly constant, is given by $\tau_c = [Q/\Delta_0 K(\infty) \mu_3(\infty) v(\tau_s)]^3 \tau_s$ [2]. The values of the time exponents η_R and η_n are thus obtained analytically at each stage and are listed in Table I.

Equation (4) is a new kinetic equation which enables us to describe the whole kinetic process from stage G to stage C. Since it does not contain any adjustable parameters, the distribution $f(R,t)$ can be determined by solving it self-consistently so as to satisfy the boundary conditions (9). In fact, by choosing a Gaussian-type initial distribution function for $F(\rho, 0)$, one can solve Eq. (4) under the initial conditions $\langle a \rangle(0) = 1.1$ and $\Phi(0) = 6.47 \times 10^{-5}$ ($Q=0.01$), 1.47×10^{-3} ($Q=0.1$), where $\Phi(0)$ is chosen so as to satisfy the conservation law (3). In Fig. 1 the time evolution of the reduced average droplet radius $\langle a \rangle(\tau)$ is shown for $Q=0.01$ and 0.1 on a logarithmic scale. In Fig. 2 we also show the time evolution of the normalized number density $v(\tau)$ for $Q=0.01$ and 0.1 on a logarithmic scale. In stage G the number density remains constant. This situation is consistent with a heterogeneous nucleation picture [1] and is different from a homogeneous nucleation picture [15]. As is seen from Figs. 1 and 2, the two crossovers are then observed in the time exponents around τ_s and τ_c . In order to confirm the theoretical results, we have also simulated Eq. (1) direct-

TABLE I. Values of time exponents.

Stage	Time exponents				
	η_s	η_K	η_R	η_n	η_Φ
G	$\frac{1}{2}$	0	$\frac{1}{2}$	0	$\frac{3}{2}$
I	$\frac{25}{36}$ (=0.694)	$\frac{2}{9}$ (=0.222)	$\frac{1}{4}$ (=0.25)	$\frac{2}{3}$ (=0.667)	$\frac{1}{12}$ (=0.083)
C	1	$\frac{1}{3}$	$\frac{1}{3}$	1	0

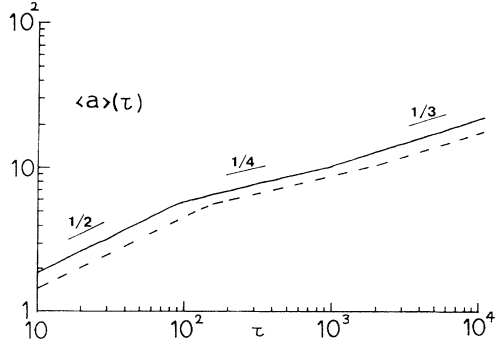


FIG. 1. Time dependence of the average droplet radius $\langle a \rangle(\tau)$ at $Q=0.01$ (dashed line) and $Q=0.1$ (solid line).

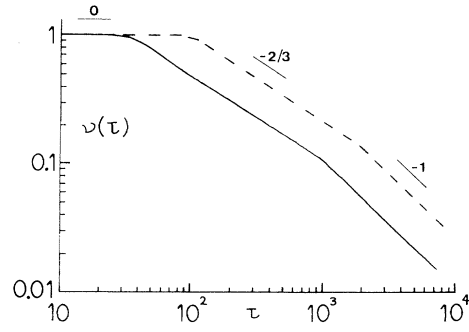


FIG. 2. Time dependence of the number density $\nu(\tau)$ for $Q=0.01$ (dashed line) and 0.1 (solid line).

ly and shown that the error introduced by the expansion in $\Phi^{1/2}$ has no effect on the first-order correction.

Starting from Eq. (1), one can also find the linear equation for the spherically averaged structure function $S(\mathbf{k}, \tau)$, to order $\Phi^{1/2}$:

$$\frac{d}{d\tau} S(\mathbf{k}, \tau) = \frac{2}{\langle a \rangle^3} [h(p, q, \tau) - \gamma(p, q, \tau)] S(\mathbf{k}, \tau) + 2 \left[\frac{4\pi\Phi}{3\mu_3} \right] \Gamma(p, q, \tau), \quad (13)$$

with the instantaneous term $h(p, q, \tau) = Z^{(1)}(p, q, \tau)$ and the damping term $\gamma(p, q, \tau) = Z^{(2)}(p, q, \tau)$, which are given by

$$Z^{(n)}(p, q, \tau) = -\frac{3}{\langle \rho^6 \psi(\rho p)^2 \rangle} \left[\langle \rho^3 \lambda J^{(n)} \rangle + \left[\frac{3\Phi}{\mu_3} \right]^{1/2} \left\{ (\beta\mu_2 - 1) \langle \rho^4 J^{(n)} \rangle - \frac{\langle \lambda^2 \rangle}{\beta\mu - 1} \langle \rho^2 I^{(n)} \rangle \right\} \right], \quad (14)$$

where $p(\tau) = |\mathbf{k}| \langle R \rangle(\tau)$, $q(\tau) = |\mathbf{k}| l(\tau)$, and

$$J^{(n)}(\rho p, q) = \psi(\rho p) \left[\omega(\rho p) - \langle \rho \omega(\rho p) \rangle \frac{2(n-1)q^2 + 1}{(q^2 + 1)^n} \right], \quad (15)$$

$$I^{(n)}(\rho p, q) = \psi(\rho p) \left[\cos(\rho p) - \langle \rho \omega(\rho p) \rangle \frac{2(n-1)q^2 + 1}{(q^2 + 1)^n} \right].$$

Here $\psi(\theta) = 3(\sin\theta - \theta\cos\theta)/\theta^3$ is the structure factor of a single droplet, and $\omega(\theta) = \sin\theta/\theta$. The source term Γ is given by

$$\Gamma(p, q, \tau) = \langle \rho^6 \psi^2 \rangle \gamma(p, q, \tau) + (3\Phi/\mu_3)^{1/2} B(p, q, \tau), \quad (16)$$

$$B(p, q, \tau) = -3[\langle \rho^4 \psi \lambda \rangle \langle \rho \omega \rangle q^2 / (q^2 + 1) + 2\langle \rho^4 \lambda J^{(1)} \rangle + (\langle \lambda^2 \rangle / \beta\mu - 1) \{ 3\langle \rho^2 \omega J^{(1)} / \psi \rangle + 2\langle \rho^2 I^{(1)} \rangle \}]. \quad (17)$$

Equation (13) is a new linear equation with the source term for the structure function $S(\mathbf{k}, \tau)$.

From the dimensional analysis of Eqs. (13)–(17), we thus find a new scaling law,

$$S(\mathbf{k}, \tau) = k_M^{-d} \Phi^{1/d} \Psi(k/k_M, \tau) \sim \tau^{\eta_s} \Psi(k/k_M, \tau), \quad (18)$$

with the peak position of $S(\mathbf{k}, \tau)$ as a function of $k = |\mathbf{k}|$ given by

$$k_M^{-1}(\tau) \sim L \sim \langle R \rangle / \Phi^{1/d} \sim \tau^{\eta_k}, \quad (19)$$

which is combined with Eq. (8) to obtain

$$\eta_k = \eta_R - \eta_\Phi/d, \quad \eta_s = d\eta_k + \eta_\Phi/d, \quad (20)$$

where $d=3$ here. The values of the exponents are listed

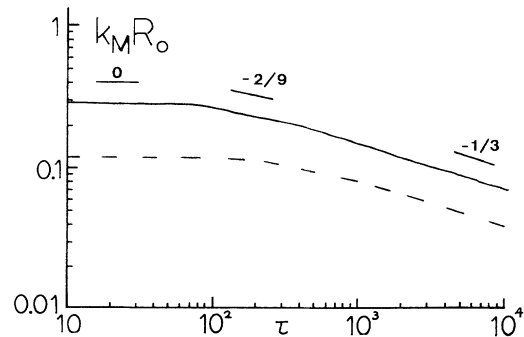


FIG. 3. Time dependence of the peak position $k_M R_0$ at $Q=0.01$ (dashed line) and 0.1 (solid line).

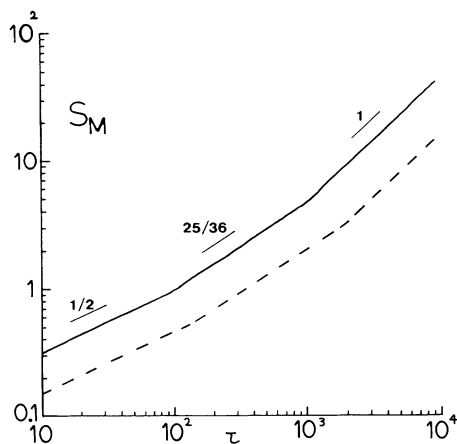


FIG. 4. Time dependence of the peak height S_M at $Q=0.01$ (dashed line) and $Q=0.1$ (solid line).

in Table I. In Figs. 3 and 4 the time evolutions of the reduced peak position $k_M R_0$ and the peak height $S_M = S(k=k_M, \tau)$ are also shown for $Q=0.01$ and 0.1 on a logarithmic scale, respectively.

The scaling relation (18) holds for the whole stage, where in stage I two lengths, $\langle R \rangle$ and L (or k_M^{-1}), are relevant, and in stage C only one length, $\langle R \rangle$, is relevant. This situation is quite different from that of the conventional theories [11–14]. The scaling function $\Psi(x, \tau)$ has the asymptotic forms

$$\Psi(x, \tau) \sim \begin{cases} x^4, & \text{for } x \ll 1, \\ x^{-4}, & \text{for } x \gg 1. \end{cases} \quad (21)$$

The x^4 dependence of the structure function for small x is caused by the nonthermal fluctuations generated by the screening interactions among droplets. This agrees with that discussed by Yeung [21–24]. The x^{-4} tail for large x , known as Porod's law, results from the fact that the droplets have sharp interfaces.

In summary, we have shown that the long-range interactions among droplets cause significant changes in the dynamics of phase separation qualitatively and quantitatively. First, the screening effect of order Φ^0 causes the qualitative change, leading to the crossover of the time exponents and the new dynamical scalings (7) and (18). Second, the correlation effect of order $\Phi^{1/2}$ alters the quantitative behavior of $f(a, \tau)$ and $S(k, \tau)$, leading to the volume-fraction dependence. Finally, we should remark that assuming that the droplets have a sharp interface at the beginning, we have derived the starting equation (1) and discussed the crossover phenomenon. This picture is confirmed by the recent experiments of Cumming *et al.* [1]. The detailed analysis of Eqs. (1), (4), and (13) will be discussed in a separate paper [2], includ-

ing their asymptotic behavior, and their dependence on Φ .

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